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The Rearrangement of Alkyl Anilines

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THE REARRANGEMENT OF ALKYL ANILINES

BY

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B.A. University of Illinois, 1914

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

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IN

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THE GRADUATE SCHOOL

June 5, 1915

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY AXEL MAGNUS HJORT

ENTITLED THE REARRANGEMENT OF ALKYL ANILINES

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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TABLE OF CONTENTS.

Page

Introduction----------1

Historical----------2

Theoretical----------8

Introduction to Experimental----------11

Experimental----------11

Purification of Propyl Alcohol----------11

The Baum Condenser (Photograph) ----------13

Preparation of Propyl Bromide----------14

Preparation of Propyl Aniline----------16

Preparation of Propyl Aniline Hydrochloride----------17

Special Apparatus (Photograph) ----------19

Description of the Bomb Furnace----------20

Bomb Furnace and Pyrometer (Photograph) ----------21

Standardization of the Pyrometer----------22

Heat Calibration of the Bomb Furnace----------22

Method of Analysis of the Rearranged Products----------24

Experiment 1.----------26

Experiment 2 ----------27

Experiments 3 and 4 ----------28

Experiment 5 (Preparation of Sulphonyl Derivative of Propyl Aniline) ----------29

Summary I ----------30

Precision of Analysis----------31

Preliminary Interpretation of the Analytical Results-----31

Summary II ----------32

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Page.
Identification of the Individual Amines of each Class-----33
The Initial Melting Points of the Sulphonyl Derivatives
of the Primary and Secondary Amines----------34
Summary III ----------34
Discussion of Summary III ----------35
Melting Points of the Purified Products----------36
Method of Crystallization----------36
Summary IV ----------36
Conclusions from Summary IV ----------37
General Summary ----------37

INTRODUCTION

In 1871 Hofmann and Martius discovered that on heating the hydrochloride of alkyl anilines in bombs, that a rearrangement took place. The resulting compounds were found to be amino alkyl benzenes. At about the same time Bardy discovered that the methyl derivatives of aniline could be applied in the dying industry. Since that time the amino alkyl benzenes have been the basis for certain aniline dyes. Little is known by the profession concerning the mechanism of the formation of these amino alkyl benzenes. It is known that amino methyl and ethyl benzenes are used in the preparation of dyes. The question then arises: Will alkyl chains of a greater number of carbon atoms, also form amino alkyl benzenes by similar rearrangements? The particular problem of this thesis is to determine whether or not amino propyl benzene acts as does the two lower alkyl compounds, and if possible to determine the mechanism of this change.

HISTORICAL

Hofmanns work on this subject dates back to 1851 when he was successful in combining an alcohol group to the aminic nitrogen atom. Hofmann and Martius performed a series of experiments on the rearrangement of methyl aniline. They prepared this substance by treating aniline with methyl bromide or iodide.Later Stass and Groves[1] obtained the same results by substituting alkyl chlorides for the bromides and iodides. In connection with the experiments on the methyl aniline,the ethyl compound was also prepared and submitted to rearrangement. No reference is made to any work on propyl aniline,in fact few of its derivatives have been made and characterized. Berthelot may have inspired Hofmann in his work,for the former,at an earlier time prepared ethyl amine hydrochloride by heating ammonium chloride and alcohol together at a high temperature.[2]

Hofmann performed his experiments with a great bulk of material,and consequently was rather superficial in his observations. In preparing methyl aniline he mixed ten kilos of crystallized aniline hydrochloride and six kilos of methyl alcohol,and submitted them to a temperature of 280°- 300°,for eight to ten hours in an autoclave. He analyzed the contents of the autoclave by steam distilling them from strong aqueous solution of sodium hydroxide,and then separating the resulting oily substance. By fractional distillation this proved to contain methyl and dimethyl aniline boiling at 200°and a small quantity of higher boiling oils. It was supposed by Hofmann that the latter were aniline compounds in which the methyl group had shifted into the benzene nucleus,after the methylation of the aminic nitrogen was

complete.

Hofmann proceeded to delve deeper into the subject,and thus procure more conclusive evidence for the substantiation of his belief as to the origin of the higher boiling oils. In his next experiment he prepared the hydrochloride of the entire prouct of the preceding operation,and submitted it,in an autoclave, to a temperature of 300° for twelve hours. By the steam distillation of this product from a strong aqueous solution of sodium hydroxide,a good yield of a basic oil was obtained,which began to boil at 210°. After drying the oil over potassium hydroxide, and then distilled,the temperature continued to rise,because of the presence of higher boiling oils,until 300° was reached. There now remained no doubt in his mind as to what had taken place,for he concluded that the methyl group rearranged itself from the aminic nitrogen atom into the ring by displacing a hydrogen atom from the latter. This theory is known as Hofmanns rearrangement of alkyl anilides.

In order to produce a proof for this theory he made various attempts to separate the products. Fractional distillation proved a failure for there was not enough of a difference between their boiling points. He then endeavored to separate them by the preparation of their salts,but to no avail,for not one of them would crystallize,with the exception of a double salt with platinum which was an incompletely crystallized substance. He then resorted to the treatment of the products with methyl iodide, which in forming the finely crystallized quarternary iodide evolved much heat. All of these iodides,were on the one hand,

because of their slight solubility in alkali,and on the other hand ,thru their convertibility into hydroxy compounds by means of silver oxide in a strong alkaline solution,easily recognized as the iodine combination of ammonia bases. He,therefore,considered the original fractions as tertiary bases. To obtain conclusive evidence,he went thru the same procedure with each individual fraction. The quarternary bases he thus procured were purified from alcohol,ether and finally water.In order to characterize his products he prepared the chlorides by treating the iodides with silver chloride. The platinum salts were obtained from the corresponding chlorides. He finally analyzed the platinum salts as well as the iodides of the ammonium bases,and thus recognized them as the salts of the tertiary amines. From these rather favorable results he advanced the following theory:-

$$C_6H_5\,N\begin{matrix}H\\H\\Cl\end{matrix} + CH_3OH \qquad C_6H_5\,N\begin{matrix}H\\H\\CL\end{matrix} + HOH$$

$$C_6H_5\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + CH_3OH \qquad C_6H_5\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + HOH$$

By further treatment with CH_3OH the methyl group was rearranged into the ring,the change,therefore,taking place in the tertiary stage as follows:-

$$C_6H_5\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + CH_3OH \qquad C_6H_4\begin{matrix}\\CH_3\end{matrix}\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + HOH$$

$$C_6H_4\begin{matrix}\\CH_3\end{matrix}\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + CH_3OH \qquad C_6H_4\begin{matrix}\\(CH_3)_2\end{matrix}\,N\begin{matrix}H\\CH_3\\Cl\end{matrix} + HOH$$

Hofmann suggests that the excess of hydrochloric acid used reacts with the methyl alcohol to form methyl chloride which is the methylating agent as Howard has definitely proven.

In the forgoing analysis Hofmann identified in addition to the tertiary methyl aniline, four other dimethyl monamines. These were evidently formed in part, by the presence of the corresponding monamines in the aniline as impurities, but mainly by rearrangement. The dimethyl monamines were as follows:-

(1) Dimethyl toluidine. $C_6H_4(CH_3)N(CH_3)_2$

(2) Dimethyl xylidine. $C_6H_3(CH_3)_2N(CH_3)_2$

(3) Dimethyl cumidine. $C_6H_2(CH_3)_3N(CH_3)_2$

(4) Dimethyl cymidine. $C_6H(CH_3)_4N(CH_3)_2$

In the light of later investigations the formation of the cymidine is questionable.

In 1872 the mechanism of the reaction between aniline hydrochloride and methyl chloride was not actually known. Hofmann and Martius[3] presumed that the methyl group at first combined with the aminic nitrogen. After the nitrogen had been completely methylated, the methyl group then proceeded to substitute itself for a hydrogen atom of the ring. In this process, therefore, no quarternary, but tertiary bases result.

Under the conditions of the experiments it was assumed that at higher temperatures and under pressure the quarternary salts were represses. To obtain the desired information Hofmann

chose the simplest compound known with which to work, trimethyl phenyl ammonium iodide. His results led him to formulate the following theory:-

The quarternary rearrange into the tertiary compounds.

$$C_6H_5N(CH_3)_2CH_3\,I + \text{Heat} \rightarrow C_6H_4N(CH_3)_2H\,I$$

The tertiary rearrange into the secondary compounds.

$$C_6H_4N(CH_3)_2CH_3\,I + \text{Heat} \rightarrow C_6H_3N(CH_3)_2H_2\,I$$

The secondary rearrange into the primary compounds.

$$C_6H_3N(CH_3)_2H_2\,I + \text{Heat} \rightarrow C_6H_2N(CH_3)_3H\,I$$

The impure product boiled at 192° - 200°. After several fractionations it distilled at 192° + 0.5°. This was the dimethyl aniline. The quarternary compound withstood 200 with little change, but on submitting it to 220 - 230 for twenty-four hours, a syrupy transparent mass resulted. At 335 (the melting point of lead) a further change took place. The contents heated to 220° to 230° when steam distilled from a strong aqueous solution of sodium hydroxide yielded a brown oil which boiled at 200° to 260.

In order to corroborate his former results Hofmann[4] in 1873 submitted the hydrochlorides and iodides of methyl aniline to 220° to 230°, and found that they did not suffer rearrangement. However, at 335° (the melting point of lead) the methyl group enter the benzene nucleus, forming toluidine. He then endeavored to obtain similar results from homologous amines. Using methyl-naphthyl amine at temperatures less than 335° , he easily obtained the

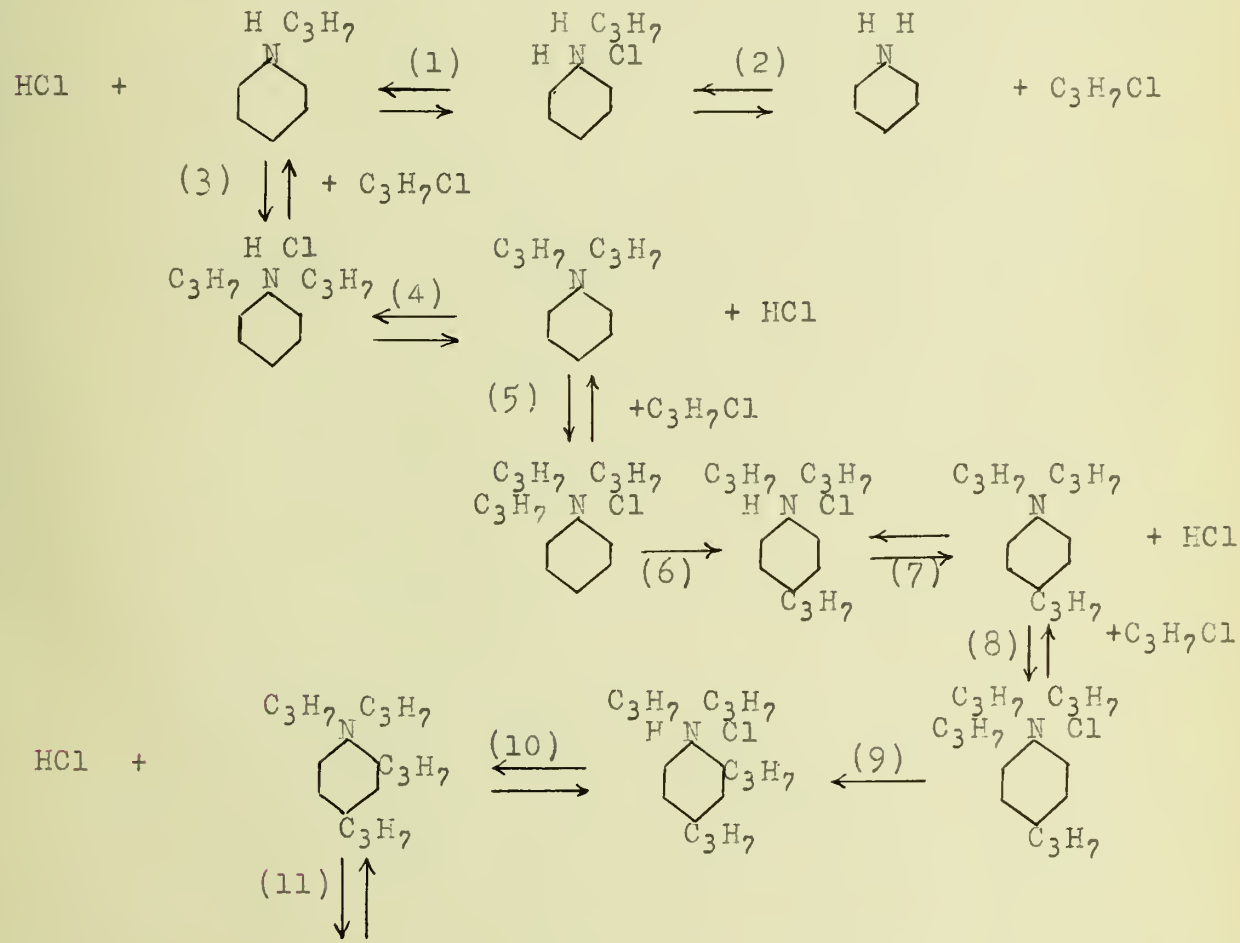
monomethyl and dimethyl naphthylamine as well as the ammonium base. At that time he did not study the mechanism of this reaction. In this connection his studies of the trimethyl phenyl ammonium iodide, led him to observe the fact that in addition to the rearrangement of the methyl groups into the primary amines, a crystalline hydrocarbon was also formed, which melted at 136° and boiled between 230° and 240°. On analysis by combustion, it proved to have the formula $C_6(CH_3)_6$.

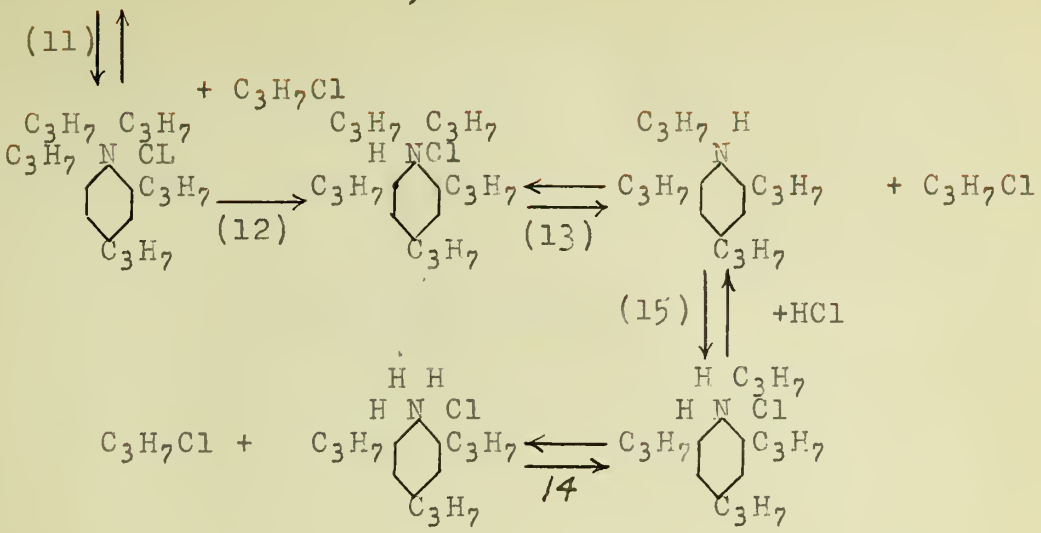
In 1874 Hofmann[5] expanded his researches so as to include other alkyl groups than the methyl. Consequently he chose the ethyl and amyl groups, and prepared the corresponding substituted anilines with which to work, in studying their action toward rearrangement from the aminic nitrogen into the benzene nucleus. His results were analogous to those he obtained with the methyl group. As a climax to this series of experiments he chose the aryl group phenyl, and expected that it would rearrange, forming amino diphenyl, but his results were negative.

THEORETICAL

The work of Howard[6] upon the behavior of methyl aniline hydrochloride at high temperatures in bombs, established the fact that an equilibrium resulted between aniline, methyl aniline and dimethyl aniline, provided that the temperature was not great enough to cause the formation and rearrangement of the phenyl trimethyl ammonium compound. Howard offered convincing evidence that the methyl chloride, formed by the dissociation of the methyl aniline hydrochloride, was the active alkylating agent in the establishment of the equilibria.

By analogy to the work of Howard on the methyl aniline, the following equilibria explains the mechanism of the rearrangement of propyl aniline hydrochloride:-





If the reactions within the bomb could be driven to completion the final products would consist of primary amino alkylated benzenes as the previous equations show. On the other hand if the temperature of the experiment was not sufficient to cause the first non-reversible reaction (6), then the condition within the bomb would be illustrated by the equilibria (1), (2), (3), (4) and possibly (5). The analytical data under Summary II, together with the data offered by Summaries III and IV give strong experimental confirmation of the establishment of these equilibria for experiments 1, 1a and 2. This is true since the primary amine has proven to be aniline, and the secondary amine propyl aniline, by the work under Summaries III and IV. Since the nature of the primary and secondary amines has been established, the analytical data of Summary II proves that the tertiary amine must be dipropyl aniline in these experiments.

Experiment 3 of Summary II showed clearly that non-reversible reaction (6), i.e. the rearrangement of the alkyl group from the aminic nitrogen into the benzene nucleus must have taken place, since a one hundred percent analysis could not be obtained

upon the assumption that the primary amine was aniline, the secondary amine propyl aniline and the tertiary amine dipropyl aniline, as was the case for experiments 1, 1a and 2. The melting points of the sulphonyl derivatives for this experiment offer further evidence for this interpretation.

This experiment in conjunction with experiments 1, 1a and 2 show clearly that the temperature at which rearrangement becomes appreciable lies somewhere between 230° and 255° for propyl aniline hydrochloride, or more correctly for phenyl tripropyl ammonium chloride, in equilibrium with the products that were discussed above.

E X P E R I M E N T A L

Introduction to Experimental.

The ensuing work is to be quantitative, and consequently it is necessary to eliminate all possible sources of error. To accomplish this end the substances to be used in the synthetic preparation of the propyl aniline were purified to the best of our knowledge. Therefore, before the thesis proper could be started, some time had to be spent in the preparation and purification of propyl alcohol, aniline, propyl bromide, and the propyl aniline hydrochloride. Various devices and apparatus had to be arranged to execute this work. After the preliminary work was finished, the propyl aniline hydrochloride was submitted to rearrangement under varying conditions of temperature and pressure.

Experimental.

Purification of Propyl Alcohol.

The propyl alcohol used was the best obtainable, but was submitted to a series of fractionations to assure its grade of purity. At first a Hahn condenser was employed, but the results were not entirely satisfactory. It was difficult to keep the temperature constant in the apparatus, altho isopropyl acetate (B.P. 90-93°) was placed in the primary condenser. It was thought that the presence of the latter substance would insure a better product of pure propyl alcohol (B.P. 97°). After the Hahn condenser was found insufficient, a substitute was sought, and discovered in the Baum condenser. This apparatus consists of a vertical chain of four condensing bulbs, with a primary condenser and side neck at the top.

This primary was half filled with isopropyl acetate to prevent the higher boiling portions of the propyl alcohol from distilling too rapidly. Superheating of the alcohol was avoided almost entirely by this apparatus,and a very pure product was obtained. A water jacketed condenser was attached to the side neck to prevent loss from noncondensation of the hot vapors.A photograph of the two forms of condensers are included in the following pages.

The purity of the various fractions was ascertained by preparing iodoform,after the boiling points had been recorded. Iodoform was made by the method of Noyes[7]. On a portion of the propyl alcohol a series of fractions was obtained,eight in number. The boiling points of these fractions were found by the distillation and the equilibrium methods. These fractions were also tested for the iodoform reaction.

-Results-

Fractions.	Boiling Points. Distillation method.	Boiling Points Equilibrium method.	Iodoform reaction.
1.	90° - 95°	93.1°	Positive.
2.	90 - 95	----	---------
3.	90 - 95	91.8	Positive.
4.	90 - 97	92.4	,,
5.	92 - 97	94.0	,,
6.	93 - 97	94.0	,,
7.	93 - 97.5	95.0	,,
8.	94 - 98	95.2	,,
9.(Residue)	95 - 98	96.8	,,

The barometric pressure during the above determinations was 745 mm.

After the purity of the propyl alcohol was known,the proper precautions were taken in the preparation of the pure product.The alcohol was now purified in large portions,as follows:- Two lots of five-hundred grams each of propyl alcohol

The Baum Condenser.

A Hahn condenser was not available, and therefore a photograph of it could not be obtained.

were submitted to distillation,and two fractions taken in both cases.The corresponding fractions were then mixed and again fractionated.

Fraction I B.P. 82°- 96.5° Yield 500 grams.

,, II B.P. 96.5°- 98.5° ,, 460 ,, .

Refractionation of fraction I produced three different portions,as follows:-

Fraction Ia B.P. 82° - 90°

,, Ib B.P. 90° - 96.5°

,, Ic B.P. 96.5°- 98.5°

After Ic had been added fraction II yielded the following:-

Fraction IIa B.P. 90° - 96.5° (Small portion)

,, IIb B.P. 96.5°- 98.5°

The yield of fraction IIb was 425 grams.

This fraction was chosen as pure propyl alcohol,containing but a trace of amyl acetate. On making the iodoform test with this substance the results proved to be positive. The latter test was made simultaneously with a similar one with isopropyl alcohol,and the outcome showed that the iso compound produced a greater yield of iodoform. This result may,however,have been due to the slowness of the reaction when the normal compound was used. Contrary to the usual statement in the literature, normal propyl alcohol gives the iodoform test as Sherman suggests.

-Preparation of Propyl Bromide-

Propyl bromide was prepared by two methods (a) the treatment of the alcohol with phosphorus tribromide,and (b) the Norris method which consists of the action of constant boiling

hydrobromic acid on propyl alcohol. The first method did not prove practicable, for the reaction was a violent one and required much time and care in its manipulation. The latter is very efficient. In the former case the yield of 78 percent of propyl bromide was obtained in one attempt. In the latter case a 96 percent yield was recovered in one trial. The Norris method[8] was used in the rest of the work. The best results were obtained from this method when four times the calculated amount of the hydrobromic acid by weight was used. This would then require eight times as much when the 48 percent acic is used.

To twenty-two hundred and twenty grams of 48 percent hydrobromic acid three portions of two hundred and ten grams each of propyl alcohol were consecutively added and very slowly distilled between 70° and 120°. The yield of the impure propyl bromide was nine hundred and fifty grams. The yield tho 73 percent, was a little low as compared with the former results. This can be readily accounted for when one considers the fact that after the first portion of two hundred and ten grams of propyl alcohol has reacted with the hydrobromic acid the proportion is not one to eight, and after the second similar portion has been converted into the bromide the ratio is again decreased: consequently each consecutive yield is correspondingly decreased.

On fractionation the propyl bromide was divided into two portions, as follows:-

Portion I Boiling point 59°-67°. Yield 200 grams.

,, II ,, ,, 67°-80°. ,, 600 ,, .

The true boiling point of propyl alcohol is 71°, there-

fore,there must have been some other substance than the bromide present. It was at first thought that isopropyl bromide was present,but this is not probable for the propyl alcohol used was practically free from the iso form. However,rearrangement could possibly have occurred from the normal into the isopropyl bromide, tho that is improbable. The solution for the trouble was finally obtained when it was discovered that a mixture of propyl alcohol and propyl bromide boiled constantly at a temperature lower than that of the latter. To remedy this tendency of the two to form a constant boiling mixture,they were refluxed for about twelve hours so as to more completely convert the alcohol into the bromide. The final yield of the bromide after refractionation was three hundred and forty-five grams,boiling at 68.5° to 72.4° . Another portion of pure propyl bromide was then prepared,and was found to boil at the same temperature as the former. The two portions when combined amounted to about seven hundred grams.

-Preparation of Propyl Aniline-

Propyl aniline hydrobromide was prepared by refluxing propyl bromide with aniline(B.P.181.4°)in molecular proportions over a steam bath for two hours. A yellow crystalline solid results,above which occurs a red liquid. The actual amounts used were as follows:-

Portion I . Propyl bromide 300 grams. Aniline 228 grams. These were refluxed for two hours and then steam distilled from a solution of potassium hydroxide(500 grams to 750 grams of water).The resulting

oil was propyl aniline. This was separated chiefly by the use of a separatory funnel, and the remainder was then extracted with ether. On fractionation it was divided into two parts:-

Ia B.P. 90° - 110° at 12 - 18 mm. pressure.

Ib B.P. 110° - 120° at 12 - 18 mm. ,, .

Yield Ib 146 grams.

Portion II. Propyl bromide 300 grams. Aniline 228 grams. These were treated as in portion I.

IIa B.P. 90° - 110° at 12 - 18 mm. pressure.

IIb B.P. 110° - 120° at 12 - 18 mm. ,, .

Yield IIb 165 grams.

In combining the two portions the total weight of the propyl aniline was three hundred and eleven grams. It is a yellow oily liquid, which decomposes at its boiling point. In former work the propyl bromide and the aniline were refluxed together for but an hour, however, more favorable results were here obtained by refluxing the mixture for two hours, and even for a longer period. Then very little red liquid was evident, and more solid material settled. The odor in the alkali after the distillation was noticibly that of a nitrile. Propyl bromide may have acted the part of chloroform in producing this effect, in the presence of the aniline.

-Preparation of Propyl Aniline Hydrochloride-

In the preparation of this compound much trouble was experienced. It took several months to devise a plan by which the propyl aniline hydrochloride could be obtained in great enough

quantity to be utilized in the work of rearrangement. The first method was that employed in the preparation of aniline hydrochloride. This consists in passing hydrochloric gas thru concentrated sulphuric acid as a drier, and then into an ether solution of the aniline. The results thus obtained were far from satisfactory, for a liquid, a semiliquid and solid portion were obtained. This mixture took weeks to dry, or become totally solid, altho it was kept in a vacuum over calcium chloride. To determine the contents of the mixture, it was analized for chlorine, by making acid with nitric acid and then adding silver nitrate.

-Results-

Liquid hydrochloride:-

3.4018 grams substance: 3.2058 grams AgCl:

Calculated %Cl. = 20.7 %, Found % Cl = 23.4 %.

Semiliquid, or nonrecrystallized hydrochloride:-

1.0253 grams substance: 0.8525 grams AgCl:

Calculated % Cl. = 20.7 %, Found % Cl = 21.09 %.

Recrystallized hydrochloride:-

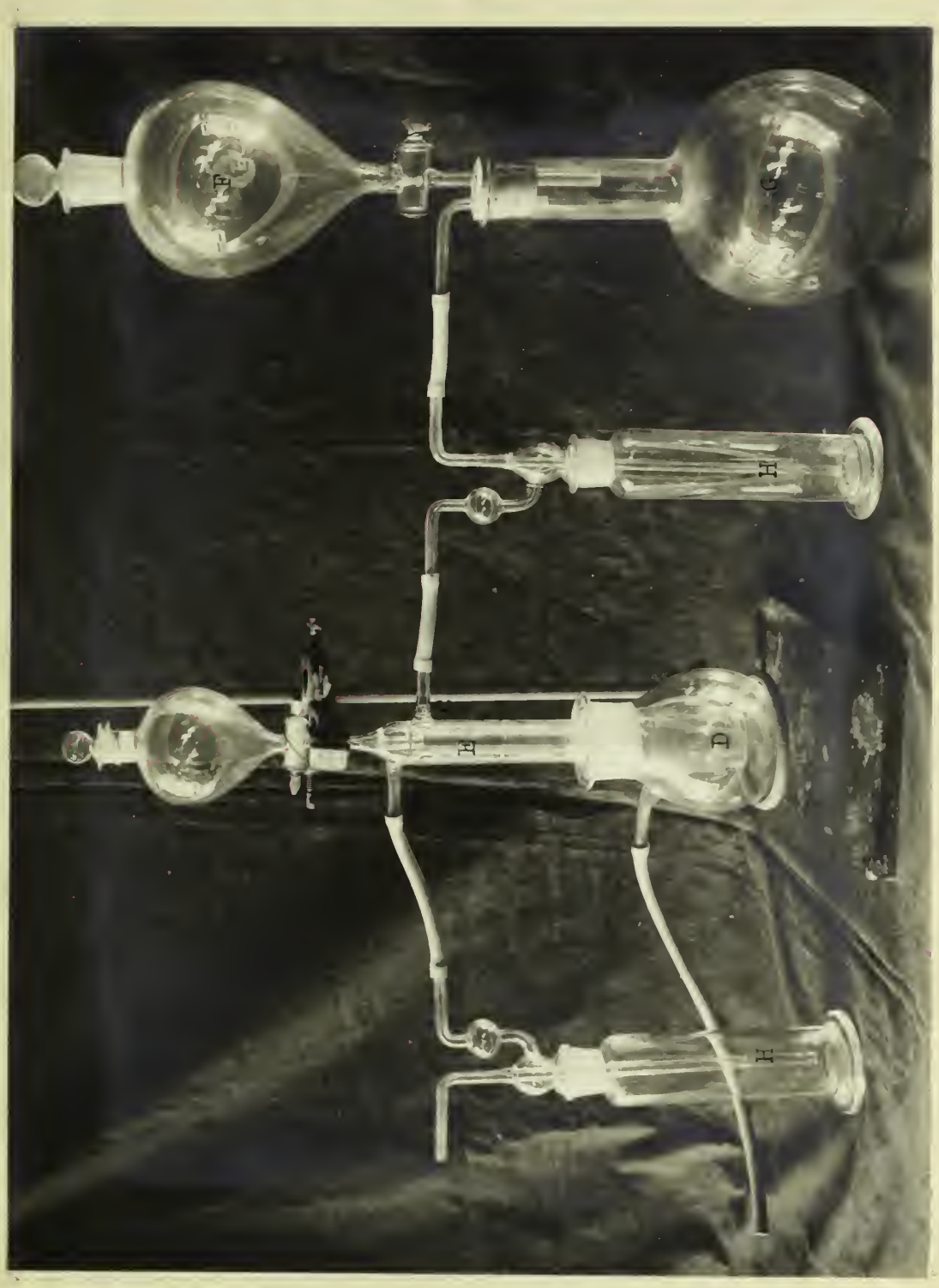
0.5136 grams substance: 0.4240 grams AgCl:

Calculated % Cl = 20.7 %, Found % Cl = 20.4 %.

From the above record it can be readily seen that they are all monohydrochlorides, but that in the case of the liquid there is an excess of hydrochloric acid.

Attempts were made to purify the liquid or crude hydrochloride by recrystallizing it from alcohol and then centrifuging. A stumbling block was again encountered, for the hydrochloride was difficult to centrifuge, in that a sticky viscous mixture resulted. This plan had to be given up and a better one

-Special Apparatus-
Used in Preparation of Propyl Aniline Hydrochloride.



A:Funnel containing ether solution of propyl aniline.
B:Air inlet. C:Hydrochloric acid gas inlet. D:Bulb in which the hydrochloride forms. E:Jacket which keeps the gas from coming in contact with ether solution too soon. F:Conc. H_2SO_4 G:Conc. HCl H:Gas and air driers. K:To suction pump.

obtained. To accomplish this a different type of apparatus would be necessary,and after some time one was found that served the purpose. The hydrochloride could then be obtained in appreciable quantities. A photograph of the latter apparatus is included with this work.

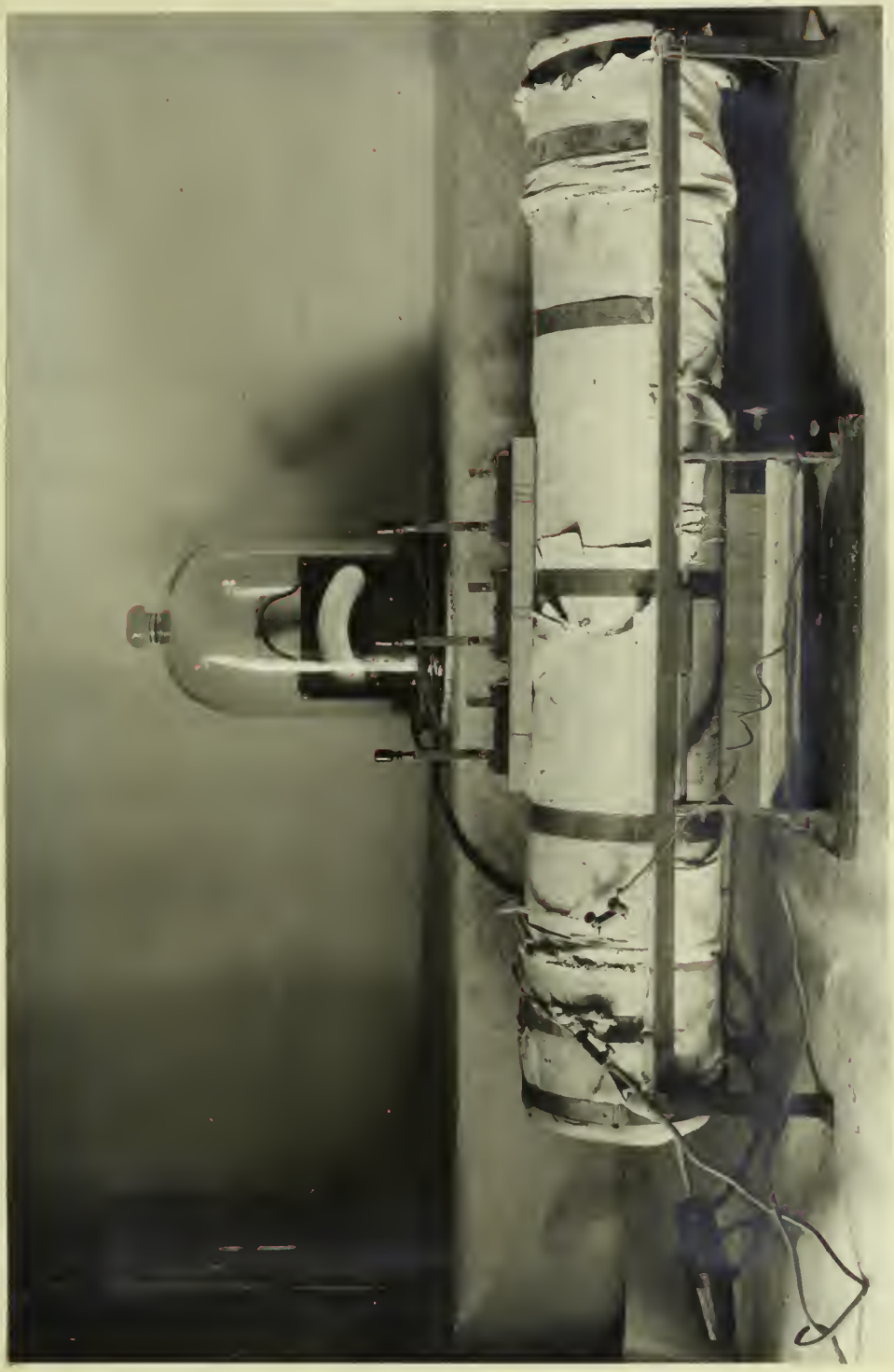
The hydrochloride melts at 142.3°.

By this method two hundred and fifty grams of the hydrochloride were prepared. This material was used in the rearrangement procedure.

-The Bomb Furnace-

The bomb furnace was made in the laboratory,and calibrated. It consists of a pipe,three inches in diameter,and thirty inches long. At one end is a solid cap which can be removed by unscrewing to permit the entrance of the bomb tubes,and at the other end there is a permanent cap with a three quarter inch hole thru which a thermocouple is inserted. The pipe is wrapped with three thicknesses of asbestos paper,and then there are threecoils of nichrome wire ten feet long alternating with similar thicknesses of asbestos paper as insulators. The outer layer or coil of wire is also covered with the asbestos,and in order to insure the best possible maintenance of heat all is encased in a steampipe covering(A mixture of magnesium and asbestos). A picture of the apparatus is included,as is the calibration.

Bomb Furnace and Pyrometer.



The description of this apparatus is found on the previous page.

Standardization of the Pyrometer.

Substances Used.	B.P.	Room Temp.	Thermometer Reading.	Pyrometer Reading. Corr.
Water	100°	25°	99.5°	99.0°
Ethylene Bromide	132	22	130.0	129.0
Anisole	155	18	155.0	155.0
Phenetol	172	18	169.0	169.0
Methyl Benzoate	199.0	22	197.5	196.5
Methyl Salicylate	224	22	221.0	220.0
Diphenyl	254.6	22	254.0	250.0

The method used in determining the above, was to place the thermocouple and a thermometer side by side in a long test-tube, and then immerse this in the vapors of the substance employed in the standardization. The temperatures registered by each were read simultaneously and recorded. From the above it is evident that the thermocouple and pyrometer record close enough for this work.

Heat Calibration of the Bomb Furnace.

Coil No.	Distance of Couple into furnace.	Amperes.	Volts.	Maximum heat.
1.	3/4	1.-1.25	102 - 110	223°
	1/2	1.-1.25	,, ,,	228
	1/4	,, ,,	,, ,,	220
2.	3/4	,, ,,	,, ,,	220
	1/2	,, ,,	,, ,,	230
	1/4	,, ,,	,, ,,	220
3.	3/4	,, ,,	,, ,,	220
	1/2	,, ,,	,, ,,	230
	1/4	,, ,,	,, ,,	220

Coil No.	Distance of Couple into furnace.	Amperes.	Volts.	Maximum heat.
1 + 2	3/4	2.2 - 2.6	102-110	374°
	1/2	2.3	,, ,,	390
	1/4	,,	90-110	377
1 + 3	3/4	,,	100	370
	1/2	,,	103	385
	1/4	2.4	107	370
2 + 3	3/4	,,	106	367
	1/2	,,	107	380
	1/4	,,	105	367
1 + 2 + 3	3/4	3.6	102	472
	1/2	,,	103	495
	1/4	,,	101	480

The coils were calibrated in order that the amount of heat that each could produce singly,in pairs and in combination of three,could be known.

Methods of Analysis of the Rearranged Products.

When propyl aniline hydrochloride was heated in bombs at varying temperatures,rearrangement occurred. The higher the temperature,within certain limits, the greater the amount of rearrangement. The method of analysis was the one devised by Howard[9]. It is in detail as follows:-

A sample of the rearranged product is carefully weighed, and to it twenty-five cubic centimeters of ten percent sodium carbonate is added. To this alkaline solution about twice the theoretical amount of benzene sulphonyl chloride is added to assure enough of the latter to react with all of the primary and secondary amines,even if the disulphonyl derivatives of the primary amines should form. After thirty minutes a one to one solution of potassium hydroxide is added to the mixture until it becomes solid. The primary sulphonyl derivatives are in the form of their potassium salts,which are insoluble in ether. On diluting with water and extracting with ether,the primary disulphonyl derivatives,the secondary sulphonyl derivatives and the free tertiary amines are recovered. After driving off the ether the latter mixture is refluxed over a steam bath,with about twenty-five grams of sodium ethylate(freshly prepared from absolute alcohol)for thirty minutes. The sodium ethylate converts the primary disulphonyl derivatives into the sodium salts of the primary monosulphonyl derivatives. The secondary sulphonyl derivatives and the tertiary amines are then removed by ether extraction of the sodium ethylate solution,which has been previously diluted with water. The secondary sulphonyl

derivatives are separated from the tertiary amines by adding hydrochloric acid,which converts the latter into the hydrochloride. This is insoluble in ether,and,therefore,the secondary sulphonyl derivatives are removed by extraction. The ether extract is then dried with anhydrous sodium sulphate,after which the ether is driven off,and the residue weighed as the secondary sulphonyl derivatives. The tertiary amines are recovered by making the hydrochlorides alkaline with sodium hydroxide,and then extracting with ether. The ether extract is treated as in the case of the secondary sulphonyl derivatives,in order to weigh the products. The two portions containing the salts of the primary sulphonyl derivatives are united and then made acid with hydrochloric acid. The primary sulphonyl compounds are then recovered from this solution by ether extraction,and subsequent drying and driving off of the ether.

After the rearrangement the bombs are opened and the contents are treated with water. The aqueous solution is extracted with ether to remove any hydrocarbons which may have been formed; the amines remaining dissolved in the water as their hydrochlorides.The primary,secondary and tertiary amines are recovered by making the aqueous solution alkaline with one to one sodium hydroxide,and then extracting with ether. The alkaline solution contains the quarternary amines,and the ether extract the remaining amines. After drying the ether extract and evaporating off the ether,the residue is the material submitted to the amine separation.

Experiment 1.

Two bombs containing twenty grams each of propyl aniline hydrochloride were heated for seven hours and a half as follows:-

Time.	Temperature.	
8.00	25°	
8.30	100	
9.00	160	Room temperature 27°.
9.30	195	
10.00	208	Bar.Pressure 747.4 mm.
10.30	195	
11.00	200	
11.30	207	
12.00	210	
12.30	208	
1.00	208	
1.30	205	
2.00	204	
2.30	204	
3.00	203	
3.30	203	

The contents of the bomb were under great pressure as was shown upon the opening of the capillary end. The odor of the gas that caused the pressure was similar to that of garlic.This gas was acid in reaction. The contents of the bombs were semicrystalline and yellow in color.

No.	Original Charge.	Bomb Volume.	Ether extract of alkaline solution.
1.	20 grams.		13.2416 grams.
2.	20 ,, .		12.9088 ,, .

Charge.	Primary Sulphonyl derivatives.	Secondary Sulphonyl derivatives.	Tertiary Amines.
1a.	3.1929 gr.	0.4802 gr.	4.5900 gr.	0.7090 gr.
b.	3.1431 ,,.	0.4620 ,,.	4.3590 ,,.	0.7560 ,,.
2a.	3.0556 ,,.	0.2750 ,,.	4.4202 ,,.	0.6276 ,,.
b.	3.0318 ,,.	0.3836 ,,.	4.3018 ,,.	0.6616 ,,.

In the above analysis all of the primary and secondary amines crystallized,some into flat rhombic and others into feather-like forms. A brownish oil adhered to the crystals in every case.

Experiment 2.

The bombs in this case were heated for seven hours and a half as follows:-

Time.	Temperature.	
10.00	25°	
10.30	110	Room temperature 25°.
11.00	190	Bar.pressure 739.8 mm.
11.30	225	
12.00	229	
12.30	229	
1.00	231	
1.30	231	
2.00	232	
2.30	233	
3.00	230	
3.30	230	
4.00	230	
4.30	229	
5.00	228	
5.30	228	

The contents of the bombs were under a high pressure. They had a strong garlic odor and gave off acid vapors. The products were more syrupy than in the previous experiment.

No.	Original charge.	Bomb volume.	Ether extract of alkaline solution.
1.	20 grams.		13.0582 grams.

No.	Charge.	Primary sulphonyl derivatives.	Secondary sulphonyl derivatives.	Tertiary amines.
1a.	6.0562 gr.	1.7056 gr.	8.4740 gr.	1.0474 gr.
b.	6.0323 gr.	1.6857 gr.	8.4795 gr.	1.0892 gr.

The weights check much better when larger amounts of the substance are used in the amine separation.

All of the primary and secondary amines in the above analysis crystallized similarly to the same compounds in experiment 1. Some had a surplus of the oily substance and therefore no melting point could be obtained for the initial product.

Experiment 3.

The bombs were submitted to heat for eight and a half hours as follows.

Time.	Temperature.	
10.00	25°	
11.00	125	Room temperature 25°.
12.00	225	Bar.pressure 745 mm.
12.30	250	
1.00	255	
1.30	245	
2.00	258	
2.30	258	
3.00	257	
3.30	257	
4.00	257	
4.30	257	
6.30	268	

The contents in this experiment were consistent yellow honey-like syrups. The higher the temperature the more completely it seems that the hydrochloride is converted to a liquid. The odor of the gas was similar to garlic. The gas was also acid as in the previous experiments.

No.	Original charge.	Bomb volume.	Ether extract of alkaline solution.
1.	20 grams.		13.2350 gr.

No.	Charge.	Primary sulphonyl derivatives.	Secondary sulphonyl derivatives.	Tertiary amines
1.	3.2180 gr.	2.2020 gr.	2.2281 gr.	0.7038 gr.

The quantity of the primary sulphonyl derivatives seem to increase directly proportional to the temperature at which the rearrangement takes place.

Experiment 4.

Attempts were made to run a series of bombs at about 300°, but in each case they exploded. The pressure is great at 200°, and increases as the temperature, and at 300° it is too great for the bomb tubes.

In experiment 3 the primary amine crystallized into transparent crystals with an oily brown coating which made it impossible to obtain its initial melting point. The secondary amine failed to crystallize.

Experiment 5.

The Preparation of the Sulphonyl Derivative of Propyl Aniline.

Three and eight-tenths grams of pure propyl aniline was weighed, and to it twenty-five cubic centimeters of ten percent sodium carbonate was added. To this mixture a slight excess over the theoretical amount of benzene sulphonyl chloride (five grams) was added and permitted to react in the cold for thirty minutes. One to one potassium hydroxide was then added to decompose the excess of the sulphonyl chloride. This solution was then diluted with water and extracted with ether. The ether extract was dried with anhydrous sodium sulphate, and then decanted off and evaporated to expell the solvent. The sulphonyl derivative of the propyl aniline thus formed was dissolved in dilute alcohol and recrystallized by scratching the side of the container with a glass rod.

The melting point of the purified product was found to be as follows:

First determination. 51.8°

Second ,, . 52.0°

SUMMARY I.

No.	Temp.	Time. hrs.	Bomb vol. cc.	Primary sulph. derivatives. (1)	(2)	(Av)	Secondary sulph. derivatives. (1)	(2)	(Av)	Tertiary Amines. (1)	(2)	(Av)
1.	200°	7.5	130	0.150	0.147	0.149	1.44	1.39	1.41	0.222	0.240	0.231
1a.	200	7.5	130	0.090	0.128	0.128	1.44	1.42	1.43	0.205	0.216	0.211
2.	230	7.5	130	0.282	0.280	0.281	1.40	1.40	1.40	0.173	0.181	0.177
3.	255	8.5	130	0.68		0.68	0.69		0.69	0.219		0.219

As is evident from the discussions of the analytic method, the primary and secondary amines are weighed as their monosulphonyl derivatives, while the tertiary amines are weighed as the free amines. Since the nature of the individual primary and secondary amines are unknown when the analyses are made, their true percentages cannot be calculated. But a check on the accuracy of this may be had by calculating the following ratios, which are tabulated above.

The primary amines:-

$$\frac{\text{Weight of the primary sulphonyl derivatives}}{\text{Weight of the charge}}$$

The secondary amines:-

$$\frac{\text{Weight of the secondary sulphonyl derivatives}}{\text{Weight of the charge}}$$

The tertiary amines:-

In this case the ratio gives the true percentage of the tertiary amines formed.

$$\frac{\text{Weight of the free tertiary amines.}}{\text{Weight of the charge}}$$

Since duplicate analyses were made upon the contents of each bomb, the ratio for these duplicates should check for a given experiment.

The first ratio in 1a. primary sulphonyl derivatives is disregarded because it differed too much from the other results, and must, therefore, have been caused by some error in the analysis.

Precision of the analysis:-

No.	Maximum deviation from the Average. (In parts)			Maximum percent variation from Average.		
	Prim.	Second.	Tertiary.	Prim.	Second.	Tertiary.
1.	2 in 149	3 in 141	9 in 231	1.3 %	2.1 %	3.9 %
1a.	------	1 in 143	6 in 211	-----	0.7 %	2.8 %
2.	1 in 281	0 in 140	4 in 177	0.4 %	0.0 %	2.2 %

These calculations show that the precision on the average is two percent, with a maximum for a single determination of five percent. This precision is very satisfactory and warrants an accuracy as great as that established by Howard, which at a maximum was not greater than six percent. This accuracy warrants the interpretation that follows:

Preliminary Interpretation of the Analytical Results.

A preliminary interpretation of the data may be made by considering the primary amine as aniline, and the secondary amines as propyl aniline, as was previously done by Howard in his work

on methyl aniline. This can be done by multiplying the ratio for the primary sulphonyl derivatives of the amines in Summary I by the fraction $\frac{\text{Molecular weight of the aniline}}{\text{Mol.weight of monosulphonyl deriv.of aniline}}$, and similarly the ratio of the secondary sulphonyl derivatives in Summary I by the fraction $\frac{\text{Molecular weight of propyl aniline}}{\text{Mol.weight of sulphonyl deriv.of propyl aniline}}$.

The fraction for aniline = 0.4
The fraction for propyl aniline = 0.49
The fraction for p.amino propyl benzene = 0.49
The fraction for nitrogen propyl amino propyl benzene = 0.56

The results of this interpretation is given in Summary II.

SUMMARY II.

No.	Temp.	Time. hrs.	Bomb vol. cc.	Primary amines. (1)	(2)	(Av)	Secondary amines. (1)	(2)	(Av)	Tertiary amines. (1)	(2)	(Av)	Summation of all Amines. In percentage.
1.	200°	7.5	130	0.060	0.059	0.059	0.705	0.680	0.690	0.222	0.240	0.231	99 %
1a.	200	7.5	130	0.036	0.050	0.050	0.705	0.700	0.702	0.205	0.216	0.211	96 %
2.	230	7.5	130	0.113	0.112	0.113	0.690	0.690	0.690	0.173	0.181	0.177	98 %
3.	255	8.5	130	0.273		0.273	0.338		0.338	0.219		0.219	83 %

In considering the primary amine as amino propyl benzene its value in experiment 3 would be increased to 3.33. the sum of the amines will then become 94%, which is more like others.

Conclusions from Summary II.

It is evident from Summary II that the experiments 1, 1a and 2 contain the monosulphonyl derivatives of primary amines, which in these cases are the monosulphonyl derivative of aniline,

and the monosulphonyl derivatives of secondary amines,which consist of the monosulphonyl derivative of propyl aniline. This must be the case since this interpretation gives a total percentage of the primary,secondary and tertiary amines of ninety-eight percent,on the average,of the initial amine charge used in the analyses. These results check those of Howard upon the rearrangement of methyl aniline hydrochloride in every detail.

In the case of experiment 3 the increase of temperature to 255°,i.e.of 25° to 55° over that for experiments 1,1a and 2,has caused a marked change in the relative proportions of the different classes of amines,due to measurable amounts of shifting of the propyl group from the aminic nitrogen into the benzene ring. In fact if the secondary amine in this experiment is still considered to be the propyl aniline,as seems most probable from its percentage,which is thirty-four percent as compared to the sixty-nine percent of the above experiments,and if the primary amine is considered to be amino dipropyl benzene,the summation of the primary,secondary and tertiary amines becomes thirty-eight plus thirty-four plus twenty-two equals ninety-four percent. These calculations give strong evidence of the fact that at 255 the propyl aniline hydrochloride rapidly undergoes rearrangement,by means of the mechanism discussed in the theoretical part

Identification of the Individual Amines of each Class.

In order to render the interpretation of the analytical results discussed under Summary II as established beyond a doubt, the melting points of the crude products had to be determined.

Initial Melting Points of the Sulphonyl Derivatives of Primary and Secondary Amines.

As noted under the description of each experiment the sulphonyl derivatives of the primary and secondary amines after standing as a rule become crystalline, thus allowing a possible interpretation of the nature of the individual amines by a study of their melting points. The melting point of each crystalline product was made after removing a few crystals to a porous plate and gently rubbing them to produce a powder. Such melting points will be called the Initial Melting Points. The results are given in Summary III.

SUMMARY III.

Sulphonyl Derivative of Primary Amine.

Exper.No.	Check No.	Melting Point.	Remarks.
1	1	108°-109°	Very free from oil.
1	2	104°	Slightly oily.
1a.	1		Too oily to melt.
1a.	2	95	Very oily.
2.	1	104	Slightly oily.
2.	2	88	Very oily.

Sulphonyl Derivative of Secondary Amine.

Exper.No.	Check No.	Melting Point.	Remarks.
1.	1	48.0°	Very crystalline.
1.	2	48.5	,, ,, .
1a.	1	47.5	,, ,, .
1a.	2	48.5	,, ,, .
2.	1		Would not crystallize.
2.	2		,, ,, ,, .

Discussion of Summary III.

Since the melting point of the pure sulphonyl derivative of aniline has been found by Keener[10] of this laboratory to be 109.3° corrected, it is evident that the primary amine fractions of experiments 1, 1a and 2 consist almost entirely of the sulphonyl derivative of aniline, as demanded by the theory of the Hofmann rearrangement. This is true since the melting points of the crude products fall within the range of the melting points recorded in the literature for this compound. The purity of the product is further demonstrated by the fact that the entire crude product crystallized in most of the experiments. In the case of experi- 3, however, the crude product would not solidify, suggesting that it is a mixture of sulphonyl derivatives of primary amines, formed by the shift of the propyl group into the benzene nucleus due to the higher temperature employed. The conclusion supports that one already drawn from the interpretation of the analytical data under Summary II.

Since the highly purified sulphonyl derivative of propyl aniline melts at 52°, the melting points of the sulphonyl derivatives of the secondary amine fractions as given in Summary III show clearly that the products consist of the sulphonyl derivatives of propyl aniline in each case, as demanded by the theory discussed in the theoretical part of this thesis. In the case of experiment 3 the sulphonyl derivative would not crystallize as was the case with the primary derivative of this experiment. This fact supports the conclusion drawn under the discussion of the primary amine, that the temperature of this experiment was sufficiently high to cause the shift of the propyl radical from the

nitrogen atom into the benzene ring.

The Melting Points of the Sulphonyl Derivatives After a Single Crystallization from Dilute Alcohol.

To render the conclusion drawn from the discussions of Summary III more conclusive each sulphonyl derivative was recrystallized from dilute alcohol in two or more fractions. The results are given in Summary IV, together with the percentage yield of each fraction, in order to estimate the percentage of a given derivative.

Method of Recrystallization.

The initial product was dissolved in as small an amount of alcohol as possible, and the water was added to dilute the resulting solution until it was necessary to apply heat to bring it in a homogeneous solution again. Then while cooling the sides of the container were scratched with a glass rod until the substance began to crystallize. After permitting the mixture to stand for a few minutes the crystals were filtered off and dried on a porous plate. When dry they were weighed, and their melting point determined.

SUMMARY IV.

Sulphonyl Derivatives of Primary Amine.

Exper.No.	Check No.	%Yield.	Melting Points.	Remarks.
1.	1	11	109.2°	Very pure.
1.	2	80	108.0	,, ,, .
1a.	1			
1a.	2	11	106.0	Slightly impure.
2.	1	41	106.0	,, ,, .
2.	2	11	106.0	,, ,, .

Exper.No	Check No.	% Yield	Melting points.	Remarks.
1.	1	83	48°	Very pure.
1.	2	76	48.5	,, ,, .
1a.	1	84	47.5	Slightly impure.
1a.	2	67	48.5	Very pure.
2.	1	46	45.5	Very impure.
2.	2	14	46.5	Slightly impure.

Melting points were taken only for the first fraction of each.

Conclusion from Summary IV.

It is obvious that this recrystallization offers strong confirmation of the conclusions drawn under Summary III. Summary IV shows that in general the yield of the first fraction of the primary amine sulphonyl derivatives is rather low, while to the contrary the yield of the sulphonyl derivatives of the secondary amines is high. This is probably due to the fact that the latter crystallize more rapidly from the dilute alcohol. It also indicates that a smaller portion of the primary compounds is aniline, than the portion of the secondary compound that is propyl aniline.

GENERAL SUMMARY.

1. This work has produced a feasible method for the preparation of propyl aniline, as well as for the preparation of pure propyl aniline hydrochloride.

2. A check has been obtained as to the accuracy with which amines could be separated quantitatively according to the method devised by Howard.

3. It was found that at temperatures below 230° no appreciable rearrangement takes place in the case of propyl aniline hydrochloride, but that between 230° and 255° rearrangement takes place

to a considerable extent. The limits of the temperature of rearrangement in bombs was also determined, for it was found that above 300° the glass bombs could not withstand the pressure set up by decomposition during the process of heating. To carry on the work under normal conditions the temperatures had to be between 230° and 300°.

4. The determinations showed that propyl aniline hydrochloride acts similar to methyl aniline hydrochloride, for its rearranged products are in every respect those predicted by the latter. The primary amine is aniline, the secondary amine propyl aniline and the tertiary amine dipropyl aniline in the experiments where the temperature was not high enough to cause rearrangement. In the case where rearrangement took place the results substantiate the theory as described in the theoretical part of this thesis.

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